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METHOD FOR PREPARATION OF CELLULOSE ETHER WITH HIGH DEGREE OF POLYMERIZATION

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A method is proposed for preparation of a water-soluble cellulose ether that is suitable for making an aqueous solution with a very high viscosity, so that it can advantageously be used as an additive to a hydraulic cement-based mortar or to a concrete composition, even while simultaneously reducing the added amount. The method consists of the reaction of raw cotton linters instead of the traditional refined linters pulp in an etherification reaction with an alkyl chloride and optionally an alkylene oxide in the presence of alkali, followed by washing with hot water and drying.

Description

The invention concerns a method for preparation of a water-soluble cellulose ether with a high degree of polymerization, which can be used as an additive to cement-based hydraulic mortar or concrete compositions, especially for continuous molding or injection molding of preformed articles.

Cellulose ethers are a class of water-soluble polymer compounds that can show a remarkable thickening effect when a relatively small amount is added to an aqueous solution or composition, so that they can be used quite commonly and

industrially in many ways as thickeners for aqueous solutions or compositions and as a water-soluble binder. Commercially obtainable and industrially usable cellulose ethers have a degree of polymerization that corresponds to a large viscosity range for a 2 wt% aqueous solution--between 3 and 100,000 cps at 20°C, which makes it possible, depending on the particular desired application, to choose a cellulose ether product to attain the desired thickening or binder effect with the addition of a suitable amount. Provided they have a high degree of polymerization, alkylcellulose ethers such as, for example, methyl cellulose, which can be prepared by the etherification of cellulose with an alkyl halide such as, for example, methyl chloride, are preferred among the various kinds of cellulose ethers as additives for hydraulic cement-based compositions.

For practical use of the cellulose ethers that have been developed in recent years, tests of a method of producing preformed articles based on hydraulic cement by extrusion are now being carried out using a cellulose ether and concrete mixtures that have consistency increased by the addition of cellulose ether in order to avoid asbestos as a reinforcing agent.

It is known that the cellulose ether that is used as additive for the above applications should have a degree of polymerization that is as high as possible, since in this way it is possible to impart to an aqueous solution a high viscosity in order to attain the desired thickening or binder effect. Here there is the possibility of reducing the added amount of the additive. For this reason there is a technical problem with regard to these water-soluble cellulose ether products to the effect of the need to develop an efficient method for the

preparation of cellulose ether that has a highly elevated degree of polymerization at low cost.

It is known that cellulose and its derivatives, including cellulose ether, is subject to a particularly significant decomposition or depolymerization under various influences such as, for example the effect of mechanical force, heating, chemicals, for example acids and alkalis, microorganisms, etc. That is why many attempts and suggestions have been made in the technology of cellulose and related products to control the degree of polymerization of the cellulose products in an appropriate way and to avoid an undesired decrease of the degree of polymerization of the cellulose products during processing.

Generally, one can make a cellulose ether product with a high degree of polymerization, to start with, by using a cellulose with as high as possible a degree of polymerization as the starting material and then by carrying out the etherification reaction under conditions that as far as possible do not give rise to any decrease of the degree of polymerization.

The traditional cellulose-containing starting material for production of cellulose ethers is refined cotton linters. The linters pulp that is obtained from refined cotton linters and that is customarily available commercially has a degree of polymerization of about 2500 to 3000, determined via the viscosity of a copper-ammonium solution--3000 to 4500 sec, measured in accordance with the A.C.S. method of a 2.5% solution in a falling ball viscosimeter. Together with the progressive technology of cotton linters refining there has recently come on the market a cotton linters product that has a higher degree of polymerization, where its copper ammonium solution has a viscosity of 10,000 to 130,000 sec, which corresponds to a degree

of polymerization of about 5000. It is now generally assumed that because of economically unacceptable costs there would be no possibility of obtaining a refined cotton linters with even higher degree of polymerization on a technical scale, although a refined cotton linters pulp can be obtained as a laboratory product that maintains its degree of polymerization from before the refining treatment.

With regard to the method for etherification of the refined starting cotton linters without a decrease of the degree of polymerization of the cellulose, the technological improvements are close to completion. They include the step of alkalinization of the starting cellulose and the reaction of the alkalinized cellulose with an alkyl halide, with the degree of etherification of the cellulose ether being highly dependent on the amount of alkali compound added for alkalinization. For a given refined starting cotton linters pulp with limited degree of polymerization it is in any case important to develop a more improved method for the etherification process of the starting cellulose material with as little as possible decrease of the degree of polymerization. Still, with the existing state of technology it is generally acknowledged that the highest viscosity, corresponding to the degree of polymerization, of a 1% aqueous solution at 20°C is approximately 20,000 cps even if the best technology is applied to refined cotton linters pulp with the highest available degree of polymerization.

For this reason a task of this invention is to make available, at low cost, a new and improved method for the preparation of cellulose ether with surprisingly high degree of polymerization, which is not obtainable by the present state of the art, where the degree of polymerization corresponds to a

viscosity of at least 20,000 cps for a 1 wt% aqueous solution at 20°C.

The inventors have carried out extensive studies with regard to this task and have come to the surprising result that a possibility of producing such a cellulose ether with high degree of polymerization that is suitable for use as an additive to a hydraulic cement-based hardenable composition lies in the use of a cellulose starting material that has not been used up to now as a starting material for cellulose ether products. Specifically, the cellulose starting material used in accordance with the invention is raw linters, which are obtained as such after the removal of the lints by separation from the cotton seeds.

Thus, the method in accordance with the invention for preparation of cellulose ethers with high molecular weight includes the following steps:

a) for carrying out an etherification reaction of cellulose 100 parts by weight raw cotton linters, with respect to the dry state, are reacted with 60 to 190 parts by weight alkyl halide in the presence of between 50 and 150 parts by weight of a basic or alkaline compound;

b) the raw cotton linters are washed with hot water after the etherification reaction; and

c) the raw cotton linters are dried after the etherification reaction and washing with hot water.

The above-mentioned etherification reaction can take place by the fact that up to 100 parts by weight of an alkylene oxide are used in combination with the alkyl halide.

As is known, the raw linters contain usually about 90% by weight α-cellulose, and the raw linters are usually subjected to a refining treatment, by which the cellulose content is raised to

about 99%. Since the refining treatment is carried out in a process that includes the boiling of the raw linters in a dilute aqueous solution of sodium hydroxide, bleaching with a chlorine bleach, for example sodium hypochlorite among others, ash removal with an acid, etc., it is unavoidable that the cellulose in the starting raw linters, which usually has a degree of polymerization of about 5000, is subjected to the effect of a progressive depolymerization. A decrease of the molecular weight to a maximum of about 2500 in the cotton linters after refining is caused by this. In order to obtain a cellulose ether product with a much higher molecular weight, in accordance with the invention the cotton linters are etherified as such in order to ensure the highest possible molecular weight before the refining treatment.

As is known, the raw linters usually contain 1 to 4% by weight contaminants, such as, for example, pectin and protein-containing substances. A problem in the investigations was that the yield of the desired cellulose ether product was not high enough or the product was colored as a result of these undesired contaminants and the relatively low cellulose content in the starting material. However, this problem can be readily compensated by the low costs of the starting material even when there is a considerable loss of yield, since the raw cotton linters are available for less than a third of the cost of refined cotton linters pulp, so that the product made from the raw linters is very much cheaper than the product made from refined cotton linters. In addition, the color of the cellulose ether products does not cause any particular problems, if care is taken to use the cellulose ether product as an additive to cement-based hydraulic compositions, since the amount that is

added is usually less than 1 wt% or less and for this reason does not have any affect on the quality or color of the cement based products.

The cellulose starting material used in the method in accordance with the invention is raw cotton linters, which is obtained after seed removal as the fluffy short fibers adhering to the cotton seeds. The raw cotton linters separated from the cotton seeds are, in contrast to the traditional refined cotton linters, used as such without carrying out a refining treatment using an alkaline aqueous solution or bleaching agent. The basic or alkaline compound used in the etherification reaction serves to dissolve the crystalline cellulose structures, which does an excellent job of accelerating the etherification reaction. It is important that the etherification reaction can be carried out completely without leaving behind a considerable amount of the alkali compound, which can give rise to a decrease of the degree of polymerization of the cellulose by a reaction as a result of its activity in combination with atmospheric oxygen. In this regard the amount of the alkali compound used for the etherification reaction is preferably 50 to 150 parts by weight per 100 parts by weight dried cotton linters and the amount should preferably not exceed 90 mol% with respect to the alkyl halide that is used.

In the method in accordance with the invention the process of etherification progresses via two different reactions, with a first reaction being expressed by the reaction equation:

$$[Cell]-OH \cdot AOH + X-R - H_2O + AX, \quad (I)$$

where for the reaction of alkali cellulose with an alkyl halide [Cell] means a cellulose residue, AOH means an alkali hydroxide, X means a chlorine or bromine atom and R means an alkyl group, and where a second reaction is expressed by the reaction equation:

$$[\mathrm{Cell}]-OH \cdot AOH + \underset{\diagdown\, O\, \diagup}{H_2C-CR^1_2} \longrightarrow [\mathrm{Cell}]-O-CH_2-CR^1_2-OH \quad (\mathrm{II})$$

where R^1 means a hydrogen atom or an alkyl group in the reaction of alkali cellulose with an alkylene oxide. These two reactions can run in competition.

Only the reaction product according to the reaction of equation (II) is soluble in hot water, so that the reaction product after completion of the reaction must be freed of contaminants by washing with an organic solvent, which unavoidably leads to an increase of production costs.

The alkyl halide used in the method in accordance with the invention is, for example, methyl chloride or ethyl chloride, which can optionally also be used together. Basically, all higher alkyl halides can be used as cellulose etherification agents, but for the method in accordance with the invention they are not appropriate, since the cellulose ether products obtained through the use of these higher alkyl halides are less soluble in water and thus are not suitable for use as additives to cement-based hydraulic compositions.

The amount of alkyl halide used in the method in accordance with the invention is in the range between 60 and 190 parts by weight per 100 parts by weight raw cotton linters in dry state. If the amount is too small, the cellulose ether product can contain a considerable amount of the unreacted cellulosic

crystalline phase, so that the solubility of the cellulose ether in water decreases, due to which the aqueous solution will not have the desired viscosity. If on the other hand the amount of alkyl halide is too high, the cellulose ether product can under certain circumstances have hydrophobic properties, which then, as a result of the reduced solubility of the cellulose ether in water, does not lead to the full viscosity of the aqueous solution.

The etherification reaction according to the method in accordance with the invention can be carried out by using an alkylene oxide in combination with the above-mentioned alkylene [sic] halide. The cellulose ether prepared by this combined use is provided with much improved water solubility. An alkylene oxide that is suitable for the method in accordance with the invention includes propylene oxide and ethylene oxide.

Any higher alkylene oxide can be used as etherification agent, but a cellulose ether product prepared by the use of such a higher alkylene oxide is less water-soluble because of higher hydrophobicity. In use the amount of alkylene oxide should not exceed 100 parts by weight per 100 parts by weight raw cotton linters, with respect to the dry state. The water solubility of the cellulose ether product cannot be further increased even by the use of an alkylene oxide in a large excess.

In the method in accordance with the invention the etherification reaction is carried out in a pressurized reaction vessel, to which the raw cotton linters are supplied as starting material. Next, the vessel is evacuated and the alkyl halide is supplied. If necessary, the alkylene oxide and the reaction mixture are agitated for several hours in the reaction vessel at a temperature in the range between room temperature and 100°C.

Optionally, the reaction mixture can be mixed with an inert solvent, such as for example dimethyl ether.

After completion of the etherification reaction the reaction mixture is washed with water, which should have a temperature of 80°C and higher for removal of the alkali halide and other byproducts and so as not to dissolve the cellulose ether. Then the residue is dried and ground or pulverized to a very fine powder, which is suitable for dissolving in water.

The method in accordance with the invention is described below in detail using examples, although the scope of the invention is not limited in any way by this. In the following description the term "parts" always refers to "parts by weight."

Example 1

In Example 1, 100 parts raw cotton linters, which contained 89.0 wt% α-cellulose, was put into an autoclave, to which after evacuation 100 parts sodium hydroxide in the form of a 49 wt% aqueous solution was added while avoiding the entry of air. Then 130 parts methyl chloride and 30 parts propylene oxide were added while agitating the mixture.

The reaction mixture was agitated in the autoclave, first at 50°C for 5 h, then at 80°C for 2 h and finally at 90°C for 1 h, in order to bring the etherification reaction to a completion. The reaction mixture removed from the autoclave was washed by adding an excess volume of hot water at 80°C or a higher temperature and dried at 105°C after separation of the aqueous wash medium. After pulverization, 110 parts of a dry powder of cellulose ether product were obtained.

The resulting cellulose ether produced a 1% aqueous solution that had a viscosity of 30,000 cps at 20°C.

Example 2

The method carried out in this example corresponded essentially to that in Example 1, with the exception that the amount of sodium hydroxide was lowered to 50 parts and 130 parts methyl chloride were replaced by 60 parts ethyl chloride and 30 parts propylene oxide were replaced by 15 parts ethylene oxide. 110 parts of a cellulose ether product that produced a 1 wt% aqueous solution that had a viscosity of 32,000 cps at 20°C was obtained.

Comparison Example 1

The processing operation was essentially the same as in Example 1, with the exception that the amount of sodium hydroxide was reduced to 40 parts and the amount of methyl chloride was reduced to 50 parts and the amount of propylene oxide was increased to 100 parts. 112 parts of a cellulose ether product that produced a 1 wt% aqueous solution that had a viscosity of 18,000 cps at 20°C were obtained.

Comparison Example 2

The method was essentially the same as in Example 1, with the exception of an increase of the amount of sodium hydroxide to 160 parts, an increase of the amount of methyl chloride to 200 parts and replacement of 30 parts propylene oxide by 100 parts

ethylene oxide. 117 parts of a cellulose ether product that produced a 1 wt% solution that had a viscosity of 15,000 cps at 20°C were obtained.

Comparison Example 3

The method was essentially the same as in Example 1, with the exception of the replacement of the raw cotton linters with the same amount of refined cotton pulp, which contained 98.5 wt% α-cellulose. 116 parts of a cellulose ether product that produced a 1 wt% aqueous solution that had a viscosity of 20,000 cps at 20°C was obtained. Thus the yield of the product obtained in Example 1 amounted to approximately 95% of the product from this comparison example.

Claims

1. A method for preparation of a cellulose ether with a high degree of polymerization, which has the following steps:

a) 100 parts by weight dried raw linters are reacted with an alkyl halide in an amount of 60 to 90 parts by weight as etherification agent in the presence of alkali in an amount between 50 and 150 parts by weight in order to etherify the cellulose in the raw linters and

b) the etherified raw linters are washed with hot water and dried.

2. A method as in Claim 1, which is characterized by the fact that a combination of 60 to 190 parts by weight alkyl halide with up to 100 parts by weight alkylene oxide is used as etherification agent.

3. A method as in Claim 1, which is characterized by the fact that the alkyl halide is methyl chloride or ethyl chloride.

4. A method as in Claim 2, which is characterized by the fact that the alkylene oxide is ethylene oxide or propylene oxide.

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	JP7119241B4	Dec. 20, 1995	Nov. 2, 1989	
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